

Photochemical Degradation of Chlorobiphenyls (PCBs)*

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Polychlorinated biphenyls (PCBs) are stable towards oxidation, hydrolysis and other chemical reactions which conceivably occur in the environment. Although there is little direct evidence available, it is generally assumed that PCBs, particularly those with a high chlorine content, are also quite resistant to metabolic change.

Over the past years photochemical degradation was shown to be a possible major route of environmental breakdown for a number of pesticides (1-4). Until relatively recently (5), however, simple chloroaromatic compounds have not received much attention. The limited interest of photochemists in compounds of this type can perhaps be explained by the commonly held view that there is generally little cleavage of the C-Cl bond in chloroaromatic compounds (6).

We have previously shown (7) that 2,2',4,4',6,6'-hexachlorobiphenyl, when irradiated at 3100 Å in hexane, photolyzes rather readily to give products which are formed by loss of chlorine, rearrangement and condensation. We now wish to present a first report of our studies on the photochemical stability of a number of chlorobiphenyl isomers in hexane as well as on the breakdown of chlorobiphenyls under natural and simulated "natural conditions", with particular emphasis on polar products.

Considerable experience in laboratory irradiations of pesticides has accumulated (1, 3, 8) and an elaborate "weathering chamber", which also allows controlled irradiation, has been described

(9). "Natural conditions", however, are difficult to simulate for water-insoluble compounds such as the PCBs. Even in sunlight, irradiation experiments in solution are artificial since "unnatural" organic solvents have to be used. Irradiations of chlorobiphenyls in thin films, in the gas phase (both in the presence of water or water vapor) or in aqueous suspension are likely to be closer to the natural environmental conditions to which PCBs are actually exposed.

Equipment and Methods

Gas chromatographic (glc) separations were carried out with a Hewlett Packard model 5750 chromatograph using a flame ionization detector and an 8 ft \times 1/4 in stainless steel column containing 3% SE-30 on acid washed Chromosorb W (60/80 mesh). Temperature was isothermal or programmed as indicated. Quantitative data were obtained with a Packard A7901 gas chromatograph equipped with a 6 ft \times 1/2 in 4% SE-30 column and an electron capture detector using the conditions previously described (10).

Combined glc mass spectral data were recorded with a Hewlett Packard model 5750 instrument, using a 6 ft \times 1/8 in glass column, coupled to a DuPont/CEC 21-491 mass spectrometer via a single stage jet separator.

A DuPont/CEC 21-110B mass spectrometer equipped with a direct introduction-constant temperature probe (11) was used for obtaining spectra of individual samples.

The infrared (ir) spectra (thin films) were recorded on a Perkin Elmer 237 spectrophotometer.

Thin-layer chromatography (tlc) was carried out on precoated Merck silica thin layer plates (F-254) and plates (100 \times 20 cm) coated with

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Merck silica gel (F-254; 0.9 mm thickness). Solvents used were: hexane and (A) 1,1,1-trichloroethane-hexane (5:1), (B) hexane-acetone (3:1), (C) benzene-ethyl acetate (12:1), (D) benzene-chloroform (2:3). The chlorobiphenyls were synthesized as described before (12,13). Aroclor 1254 was a gift of Monsanto Co.

Sources of ultraviolet light for the irradiation experiments were as follows:

- (i) Sun: direct sunlight at Halifax, N.S. during the period July to September 1971.
- (ii) Photochemical reactor: Rayonet (the Southern N.E. Ultraviolet Co.) using 16 R.P.R. 3100 lamps (3100 Å). The temperature was maintained at $14 \pm 2^\circ$.
- (iii) Blacklight: four General Electric F40BL fluorescent lamps mounted with reflective backing ca. 15 cm above the samples. The temperature at this distance was $30\text{--}33^\circ$.
- (iv) Sunlamp: General Electric 275 W "Sunlamp", one per dish at ca. 25 cm distance (temp. $35\text{--}40^\circ$). For irradiation of chlorobiphenyl/water vapor, four lamps per 500 ml quartz tube were mounted horizontally at ca. 10 cm. distance.

Experiments and Results

Stabilities of Chlorobiphenyls at 3100 Å in Hexane Solution

Time study of 2,2',5,5'-tetrachlorobiphenyl decomposition—2,2',5,5'-Tetrachlorobiphenyl (50 mg) in hexane (300 ml) was irradiated in the Rayonet reactor with N_2 bubbling through the solution. 50 ml Aliquots were removed from the reaction vessel at 2, 4.5, 17, 41 and 89 h. Good quantitative data could not be obtained for the 89 h sample, probably because much of the material had polymerized. Chromatograms observed after injecting equal amounts of these aliquots and using a flame ionization (F.I.) detector are shown in Fig. 1. Percentages of starting material remaining after different irradiation times are also presented in Fig. 1. These data were obtained by measuring the area under the peak with retention time identical to the starting material

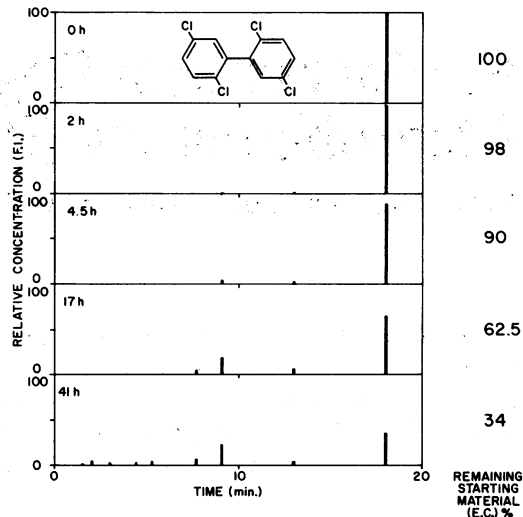


FIGURE 1. Irradiation of 2,2',5,5'-tetrachlorobiphenyl for different times; chromatograms and percent starting material remaining.

using an electron capture (E.C.) detector. Mass spectral and glc data for the 41 h sample are given in Fig. 2.

Comparative stability of chlorobiphenyl isomers—A 0.1% solution (3 ml) of the chlorobiphenyl hexane was flushed for 3 min with nitrogen, stoppered and irradiated in the Rayonet reactor for 24 h. The volume of the solution was removed from the quartz reaction cell and, after rinsing with hexane and evaporation of some of the solvent, adjusted to 3 ml. Equal amounts of the irradiated solution and the original solution

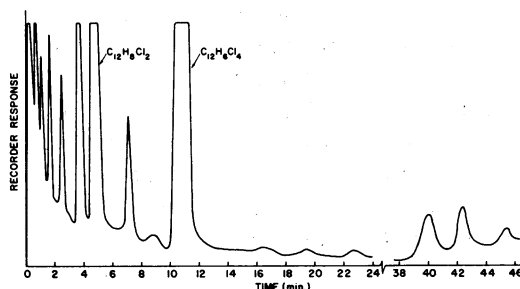


FIGURE 2. Chromatogram and mass spectral data for the 41 h sample. Oven temperature 150° isothermal, at 36 min beginning of programming ($4^\circ/\text{min}$). A number of further peaks were observed after 46 min.

Table 1. Relative Photochemical Labilities of some Chlorobiphenyl Isomers

Compound	Starting material remaining after 24 h at 3100 Å in Hexane
Tetrachlorobiphenyls	%
3,3',4,4'-	32
2,2',6,6'-	29
2,2',5,5'-	33
2,2',4,4',5,5'-	3.8
Hexachlorobiphenyl	
2,2',3,3',4,4',5,5'-	<1
Octachlorobiphenyl	

were injected into the gas chromatograph, and the areas under the peak corresponding to the starting material compared (Table 1). No immediate correlation can be seen between steric hindrance of *o*-chlorine substitution or uv spectra (14) and photochemical lability, although chlorobiphenyls with high chlorine content seem to degrade more rapidly.

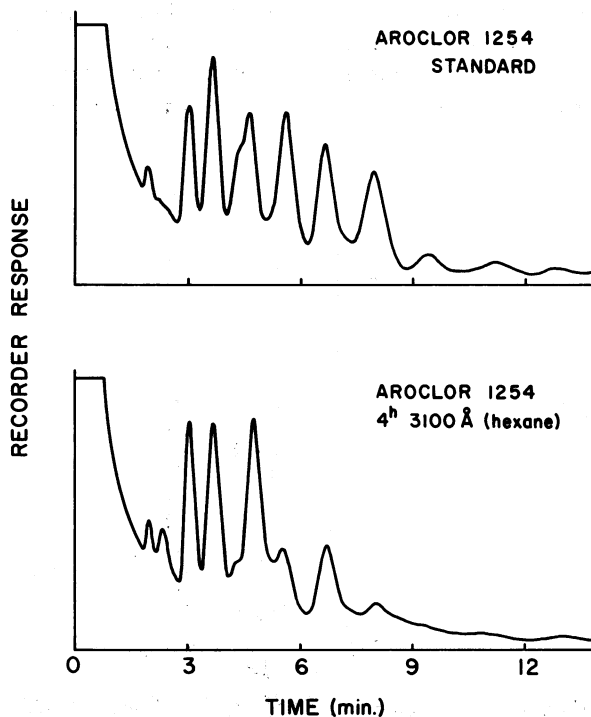


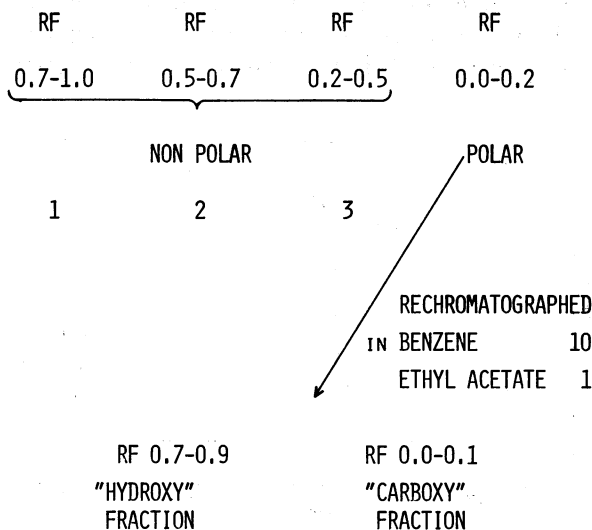
FIGURE 3. Chromatogram of Aroclor 1254 before and after irradiation. Glc conditions of (10).

Stability of Aroclor 1254—Aroclor 1254 (20 mg) in hexane (3 ml) was irradiated for 4 h at 3100 Å in the presence of air. Examination of the irradiated mixture and standard Aroclor 1254 by glc shows gross differences with tendencies toward shorter retention times (Fig. 3).

Irradiations in Sunlight; Under Simulated "Natural" Conditions and in Solvent Mixtures Containing Water

Aroclor 1254 I; Aqueous dioxane suspension at pH 9—A suspension of Aroclor 1254 (2 g) in a mixture of dioxane (150 ml) and water (350 ml) containing sodium bicarbonate (0.5 g) was irradiated in the Rayonet reactor for 24 h with air bubbling through the mixture. After this period another portion of sodium bicarbonate (0.5 g) was added, and the irradiation continued further for 24 h. The mixture was worked up as shown in Scheme 1. Preliminary mass spectral data for the crude nonpolar fractions one, two and three indicated the presence of only chlorobiphenyls since no ions containing oxygen corresponding to hydroxychlorobiphenyls or chlorodibenzofurans were detected. The mass spectrum of the crude

CHLOROBIPHENYL EXPOSED TO UV, EXTRACTED WITH ETHER AT pH2, PREPARATIVE TLC (2X HEXANE)



SCHEME 1. Separation-scheme for irradiated chlorobiphenyls.

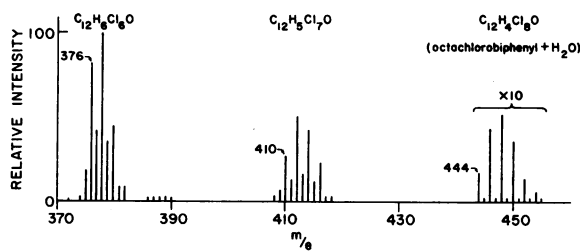


FIGURE 4. Partial mass spectrum (70 eV; probe temperature 35°) of "hydroxy" fraction from Aroclor 1254 irradiation experiment I. The chlorine isotope pattern for the Cl_6 and Cl_7 compounds are distorted due to impurities or fragment ions.

"hydroxy" fraction, part of which is shown in Fig. 4, indicated the presence of compounds formed by the addition of water to chlorobiphenyls. Hydroxy and carbonyl stretching frequencies in the infrared spectrum of the crude "carboxy" fraction (Fig. 5) are indicative of the type of compounds present in this mixture.

Aroclor 1254 II; Irradiation as thin film—Aroclor 1254 (0.5 g) was dissolved in benzene (3 ml), and this solution spread over a circular pyrex dish (diameter: 35 cm). The benzene was allowed to evaporate slowly in a way to ensure formation of a uniform Aroclor 1254 film. Water (3 ml) was added, and the dish was covered with plastic film. Water was frequently replaced during the Blacklight one-week irradiation. The irradiated product was fractionated according to Scheme 1. Preliminary mass spectra of the crude nonpolar fractions 1 and 2 (in this experiment no material

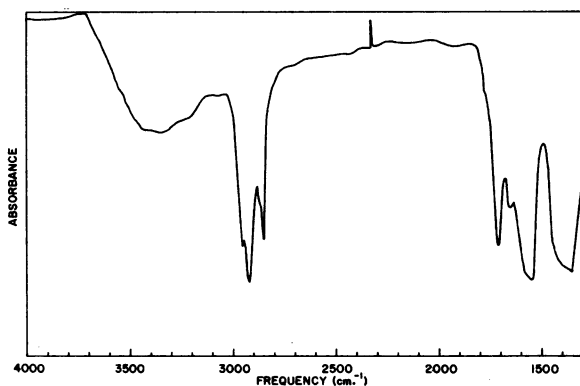


FIGURE 5. Partial infrared spectrum (thin film) of "carboxy" fraction from Aroclor 1254 irradiation experiment I.

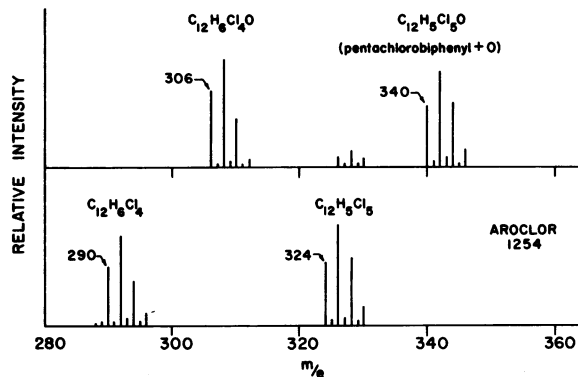


FIGURE 6. Partial mass spectra (70 eV; probe temperature 35°) of "hydroxy" fraction from Aroclor 1254 irradiation experiment II (top) and standard Aroclor 1254 (bottom; ions <340 not shown).

corresponding to 3 was detected) showed only the presence of chlorobiphenyls. A mass spectrum of the crude "hydroxy" fraction (Fig. 6) showed ions which can be most easily explained as resulting from hydroxychlorobiphenyls. The ir spectrum of the crude "carboxy" fraction was almost identical to that from experiment I (Fig. 5).

Irradiations of 2,2',5,5'-tetrachlorobiphenyl—Some information on the types of products formed from 2,2',5,5'-tetrachlorobiphenyl on irradiation under a variety of conditions is given in Table 2. Samples were fractionated as

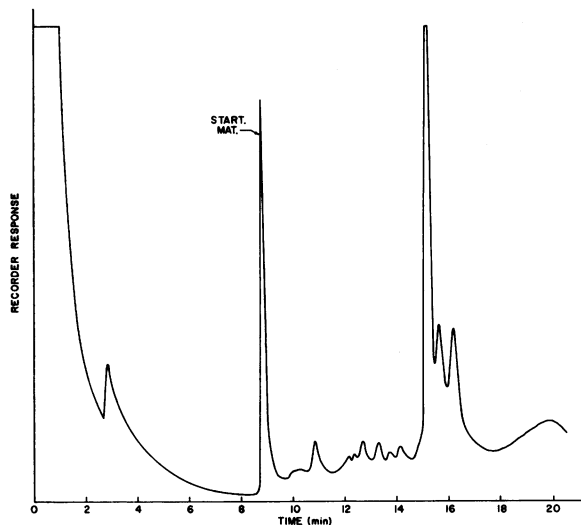


FIGURE 7. Chromatogram for 2,2',5,5'-tetrachlorobiphenyl irradiation experiment II. Oven temperature programmed from 150° at 10°/min until 310°. A number of further peaks were observed after 20 min.

Table 2. Photochemical Decomposition of 2,2',5,5'-Tetrachlorobiphenyl.

Experiment number	Irradiation conditions	UV source	Time	Types of products formed ^{a,b}			
				"Polar" products		"Nonpolar" products	
						Retention time ^c	
				"Hydroxy-"	"Carboxy-"	Short	Long
1	Aqueous suspension (+ emulsifier)	sun	2 mo	—	+	(+)	+
2	Thin film	sun	2 mo	(+)	+	(+) ^d	+ ^d
3	Thin film	sun lamp	24 h	(+)	+	(+)	+
4	Thin film	black light	1 wk	(+)	+	(+)	+
5	Dioxan-2N NaOH solution	reactor	16 h	—	+	+	+
6	Aqueous dioxane solution + FeCl ₃	reactor	16 h	(+)	+	+	+
7	Vapor (refluxing with water)	sun lamp	16 h	—	+	(+)	+

^a + = present; (+) = present in small quantities; — = not detected.

^b For further description of products, etc. see text.

^c Glc retention time shorter or longer than starting material (2,2',5,5'-tetrachlorobiphenyl).

^d See Fig. 7.

described in Scheme 1. The nonpolar fraction was analyzed by glc (e.g. Fig. 7).

"Carboxy"-type compounds were indicated in all experiments by the chromatographic properties of a portion of the reaction products which were similar to the corresponding fractions from the Aroclor 1254 irradiation experiments I and II (i.e., $R_f < 0.1$ in solvents A-C; high R_f in aqueous methanol mixtures).

The presence of "hydroxy"-type compounds was indicated by:

- (i) chromatographic comparison of the appropriate fractions with authentic hydroxy- and dihydroxybiphenyls in solvent systems A, (R_f 0.3–0.8); B, (R_f 0.3–0.7) and C, (R_f 0.4–0.8), and
- (ii) by reacting the "polar" fractions with dansyl chloride (1-dimethylaminonaphthalene-5-sulfonyl chloride) and comparing the chromatographic properties (solvent D; R_f ca. 0.75 for monohydroxy and ca. 0.4 for dihydroxy compounds) and in situ fluorescence excitation (350 nm) and emission (525 nm) wavelength

with those of dansyl derivatives of authentic hydroxy and dihydroxybiphenyls (see reference 15 for the general method).

Discussion

The photolysis of chlorobiphenyls reveals a number of degradative reactions which occur on irradiation in sunlight and a number of laboratory conditions. In hexane, the most prominent reaction was the progressive reductive dechlorination of these compounds as well as formation of polymeric materials. Irradiation of Aroclor 1254 in hydroxylic solvents at pH 9 yields compounds corresponding to the addition of water to the PCB molecules and a more polar carboxylic acid fraction. The same sample irradiated as a thin film does not yield the water-addition products, but mass spectrometry reveals the presence of new hydroxylated species. This experiment also gives a more polar "carboxylic" fraction. Data for a number of different irradiations of 2,2',5,5'-tetrachlorobiphenyl indicate that dechlorination, formation of polymers, and carboxylic products as well as hydroxylation, does occur.

The present photolytic work thus reveals decomposition of PCBs by both oxidative and reductive pathways.

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